# Response surface applied to optimize prednisone removal in aqueous medium by photo-assisted peroxidation ($H_2O_2$/UV)

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The growing presence of micropollutants in aquatic environments can lead to serious impacts on human health. The peroxidation process presents itself as an effective alternative for treating these compounds. This work studied the efficiency of the $H_2O_2$/UV process for degrading prednisone in an aqueous media. A composite design (CCD) was employed to evaluate the efficiency of the influence of the control variables $H_2O_2$ concentration (44.2 to 126.6 mM) and UV radiation intensity ($5.99\times10^{-7}$ to $3.40\times10^{-6}$ einstein.s$^{-1}$). Among the experiments, those carried out at the central point ($H_2O_2$ = 84.4 mM; UV Rad. = $2.0\times10^{-6}$ einstein.s$^{-1}$) provided the best results for TOC reduction, ranging from 43.18 to 44.71%. Statistical analyses identified the optimal treatment condition (84.4 mM for $H_2O_2$ and $2.7\times10^{-6}$ einstein.s$^{-1}$ for UV radiation), predicting a theoretical TOC reduction response of 44.62%, experimentally validated with a real reduction of 44.69 ± 0.34%.

## Introduction

Numerous environmental studies have demonstrated that organic micropollutants can be present in various parts of the ecosystem, such as soil and aquatic environments. The presence of these compounds poses serious risks to humans and animals, primarily due to inadequate disposal practices and limitations of conventional wastewater treatment methods [1-2].

Pharmaceuticals are a major source of these environmental contaminants due to both increasing use and improper disposal [1-2]. Corticosteroids, such as prednisone, are examples of this, particularly due to their low aqueous solubility and low absorption by the human body [3].

In this context, the photo-assisted peroxidation process ($H_2O_2$/UV) emerges as a treatment alternative for these types of contaminants, as it can promote the degradation of organic matter due to the action of highly reactive hydroxyl radicals [2].

Therefore, this study aimed to determine the best experimental condition to maximize the reduction of total organic carbon (TOC) from an aqueous reaction medium containing prednisone.

## Material and Methods

The prednisone used was of micronized HPLC grade and the other reagents were of analytical grade.

The reaction medium consisted of an aqueous solution of prednisone at 60 mg.L$^{-1}$ and pH of 7.5. Batch assays were conducted using a quartz annular photochemical reactor with 5 and 7 W lamps from Osram Puritec HNS G23 arranged internally and/or externally to the photoreactor, emitting UV radiation at 253.9 nm. A uniform radiation field was assumed. The reactor was connected to a mixing tank where the medium was recirculated (1 L.min$^{-1}$), from which samples were taken. The total volume of the reaction medium was 500 mL and the effective volume of the irradiated reactor was 70 mL for 60 minutes. All experiments were conducted at room temperature.

These experiments were carried out using a Central Composite Design (CCD) $2^2$, with 4 corner points, 4 axial points, and triplicates at the central point, totaling 11 experiments. The control variables were $H_2O_2$ concentration (44.2 to 126.6 mM) and UV radiation ($5.99\times10^{-7}$ to $3.40\times10^{-6}$ einstein.s$^{-1}$), and the response evaluated was the reduction of TOC.

TOC was analyzed by controlled combustion at 680°C with platinum catalyst, using a Shimadzu Analyzer, Model TOC-VCPN, as established in the Standard Methods of Examination of Water and Wastewater.

## Results and Discussion

The CCD aimed to optimize the photo-assisted peroxidation process. Table 1 presents the TOC reduction results for each experiment.

The experiments conducted at the central point ($H_2O_2$ = 84.4 mM; UV Rad. = $2.0\times10^{-6}$ einstein.s$^{-1}$) achieved the highest TOC reduction, ranging from 43.18 to 44.71%.

To assess the level of influence of the control variables on the response variable TOC (%), the results were statistically evaluated at a confidence level of 95% using Statistica® software. The Pareto diagram and the response surface are shown in Figures 1 and 2, respectively.

Upon analyzing the Pareto chart (Figure 1), it was observed that the control variable UV radiation and the quadratic interaction of $H_2O_2$ were statistically significant for TOC reduction, as the calculated t values exceeded the tabulated value (2.5706).

From an experimental perspective, it can be stated that the action of UV radiation combined with the presence of $H_2O_2$ was effective in generating hydroxyl radicals, which were more active in degrading organic matter.

**Table 1.** Experimental matrix and results obtained from the photo-assisted peroxidation process.

| Exp | UV radiation ($.10^7$ einstein.$s^{-1}$) | $H_2O_2$ (mM) | COT (%) |
|---|---|---|---|
| 1 | 10.1 (-1) | 54.5 (-1) | 26.89 |
| 2 | 29.9 (+1) | 54.5 (-1) | 39.19 |
| 3 | 10.1 (-1) | 114.3 (+1) | 29.62 |
| 4 | 29.9 (+1) | 114.3 (+1) | 33.82 |
| 5 | 20.0 (0) | 42.2 (-1,41) | 17.84 |
| 6 | 20.0 (0) | 126.6 (+1,41) | 23.77 |
| 7 | 5.99 (-1,41) | 84.4 (0) | 16.91 |
| 8 | 34.0 (+1,41) | 84.4 (0) | 36.81 |
| **9** | **20.0 (0)** | **84.4 (0)** | **43.18** |
| **10** | **20.0 (0)** | **84.4 (0)** | **44.71** |
| **11** | **20.0 (0)** | **84.4 (0)** | **43.69** |

(1) The values in parentheses represent the respective levels of the experimental design: (-1) low, (0) central point, (+1) high, and axial points (-1.41 and +1.41).

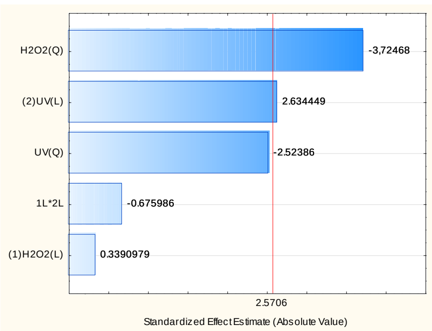


**Figure 1.** Pareto chart for TOC reduction.

Higher amounts of $H_2O_2$ (exp. 6 - 124.4 mM) compared to the central point (84.4 mM) did not significantly increase TOC reduction, which may be due to the excess $H_2O_2$ scavenging the formed hydroxyl radicals and/or forming less effective radicals in degradation.

The photon flux established at the central point ($2.0\times10^{-6}$ einstein.$s^{-1}$) was sufficient for hydroxyl radical formation, as higher values (exp. 8: $3.4\times10^{-6}$ einstein.$s^{-1}$) did not enhance the effect.

As shown in Figure 2, the optimal treatment region (TOC > 40%) falls near the central condition of the CCD (UV Rad. = $2.0\times10^{-6}$ einstein.$s^{-1}$ and $H_2O_2$ = 84.4 mM). By utilizing the Desirability function in the Statistica® software along with the proposed mathematical model (Equation 1), the optimal conditions were determined for prednisone degradation through this process, which were 84.4 mM for $H_2O_2$ and $2.7\times10^{-6}$ einstein.$s^{-1}$ for UV radiation. Under these predicted optimal conditions, the model predicted a TOC reduction of 44.62%.

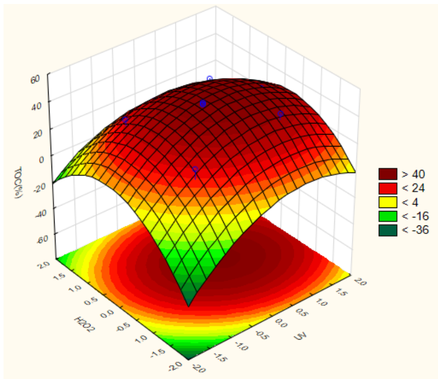


**Figure 2.** Response surface for TOC reduction.

$$TOC\ (\%) = 43.86 + 5.58\times UV + 0.72\times H_2O_2 - 6.36\times UV^2 - 9.39\times (H_2O_2)^2 - 2{,}02\times UV\times H_2O_2 \quad (1)$$

With these results, duplicate experiments were conducted under optimal conditions, and an average reduction in TOC of 44.69 ± 0.34% was observed. This result confirms that the proposed mathematical model accurately represents the photo-assisted peroxidation process within the studied range of control variables.

## Conclusions

The use of response surface as a technique for optimizing prednisone degradation by photo-assisted peroxidation has proven to be an effective tool for determining the optimal treatment condition. Additionally, the use of this advanced oxidative process demonstrated significant capacity to remove approximately half of the organic load present in the reaction medium (44.69 ± 0.34%), due to the presence of this corticosteroid.


### *Acknowledgments*

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